PRESENTATION FOR EPA STATISTICS CONFERENCE (DRAFT 03/05/91)

In 1988, EPA and the paper industry conducted a cooperative study to evaluate the discharge of dioxin and furan from all mills in the U.S. which bleached wood pulps with chlorine or chlorine derivatives. There were 104 of these mills; and the study was called the "104-Mill Study". The study was limited to these mills because other studies have shown that the bleaching of wood pulp with chlorine is a source of dioxins and furans. The goal of the cooperative study was to measure dioxin and furan levels in samples of effluent, sludge, and pulp from the mills. The dioxin and furan levels were measured using a high resolution GC/MS and isotope dilution analytical procedure developed by the paper industry for the most toxic of the dioxin and furan congeners: 2,3,7,8-TCDD and 2,3,7,8-TCDF. The effluent samples were taken of treated or untreated wastewater depending on the mill's facilities for wastewater treatment. There were very few untreated wastewater samples. The sludge samples came from semi-solid residue from the treatment system. The pulp samples were cellulose fibers after conversion from wood chips. The effluent, sludge, and pulp samples were collected in mid to late 1988. Industry played a big role in this cooperative study. Industry managed the study and provided EPA with the results of the laboratory analyses.

In this presentation, I will focus on seven conclusions we reached in our analysis. The first five conclusions apply to effluent, sludge, and pulp. However, I will only present the findings for effluent. The first conclusion is that detected values appear to be lognormally distributed. The second conclusion is that the non-detect measurements can be modeled by a log-regression method. The third conclusion is that target detection levels of 10 ppq for effluent and 1 ppt for sludge and pulp are achievable. These target detection levels were established as goals at the beginning of the study. As part of this study, a number of lab and field duplicates were collected. The next two conclusions are based on the analysis of those duplicates. These conclusions are that analytical variability is relatively low based on the analysis of laboratory duplicate samples, and based on the analysis of field duplicates, variability due to the combined field sampling and analytical error is relatively low. The last two conclusions out of the seven apply to the combined output from effluent, sludge, and pulp, but only the results for TCDD will be presented. The sixth conclusion is that greater chlorine use is associated with higher TCDD and TCDF discharges from the mills. The last conclusion is that increased chlorine dioxide substitution for chlorine is associated with slight reductions in TCDD and TCDF.

As I mentioned before, as part of the cooperative agreement, industry agreed to collect the data and send the results to EPA. The National Council of the Paper Industry for Air and Stream Improvement (called NCASI) managed the program for industry. NCASI provided guidance on taking the samples, developed the laboratory method, submitted the samples to labs and reviewed the results before forwarding them to EPA. NCASI's analytical method 551 which was used in the laboratory analyses is similar to EPA's method 1613 for analyzing dioxins and furans. Both are high resolution GC/MS methods. The main difference between the two methods appears to be that NCASI's method is limited to the analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF. The EPA method was designed for the analysis of all 17 2,3,7,8-substituted PCDDs and PCDFs. Other differences between the two methods are in the extraction procedures and the sample clean-up techniques.

Each mill was required as part of the agreement to provide one sample from each of effluent, sludge, and fully bleached pulp. These samples were composite samples taken over a 5-day period. This generated about 400 samples with about 80 additional samples for QA/QC. The mills also submitted process information corresponding to the dates of sampling. EPA also received from NCASI a limited amount of QA/QC information (recoveries and ion ratios). Based on NCASI results from an inter-laboratory study, the paper industry decided that too much variability would be introduced by using different labs and decided to use only two labs. Both labs did some samples from each of effluent, sludge, and pulp; however, the bulk of the analyses for any particular matrix was limited to one lab. The two labs were Wright State University in Dayton, Ohio which did about 80% of the pulp analyses. Enseco-California Analytical

Laboratories in West Sacramento, California was the other lab and did 89% of the effluent samples and 81% of the sludge samples. There were not enough samples done by both labs to estimate inter-laboratory variability.

The presentation's emphasis will be on TCDD concentrations in effluent at kraft mills. There are several reasons we chose to focus on effluent in this presentation. The conclusions based on analyses of effluent data are similar to those based on sludge and pulp data. In addition, there were confounding factors in the measurements of sludge and pulp which are not present in effluent. In some cases, the sludge samples were difficult to obtain physically, and the results may not indicate the effectiveness of the treatment system. Pulp is the final product rather than a by-product as are effluent and sludge. Pulp was collected earlier in the process than effluent and sludge. The pulp was sampled before going through the drying process and the water from this drying process became part of the effluent which was then sampled later. This may have resulted in some double-counting of TCDD and TCDF levels between pulp and effluent.

We also decided to focus on the results for TCDD for this presentation. This graph shows the strong relationship between TCDF and TCDD for effluent from kraft mills. The linear regression of this relationship gives an R^2 of 79%.

In addition, we're focusing on kraft mills for a number of reasons. The processes at kraft and sulfite mills are very different and in our analysis, we found a significant difference in the data from the two types of mills. Sulfite mills tend to produce less TCDD and TCDF because they use less bleaching than kraft mills and most of the values from sulfite mills were around the detection level. In addition, sulfite and kraft mills tend to use different types of wastewater treatment, which would affect the observed concentrations. There were also difficulties with the TCDD and TCDF analyses of samples from sulfite mills. Part of that was due to the low levels of TCDD and TCDF in the sulfite samples, and part of that was due to analytical interference. Therefore, we decided to concentrate on TCDD in effluent from kraft mills in this presentation.

Our first conclusion is that we found that the detected values appear to be lognormally distributed. In our analysis, we used logarithms of the detected measurements. This probability plot shows that the data are approximately lognormal.

For our second conclusion, we compared a number of different methods for treating the non-detected values including the delta distribution, maximum likelihood, and setting the non-detects to half the detection limit. We performed sensitivity analyses on the different methods for treating non-detects, and there did not appear to be much difference between methods. However, in general, the log-regression method seemed to be the best method for modeling data that included non-detected values in effluent, sludge, and pulp. The treatment of non-detect values is important since 28% of the effluent samples in kraft mills were non-detects for TCDD. Because all of the mills had detected concentrations in either effluent, pulp, or sludge for TCDD or TCDF, we concluded that a non-detect was more likely to be an amount too small to measure rather than an indication that the TCDD and TCDF were not in the sample. In the last plot, there was a slight curve at lowest levels. This curve seems to be due to the exclusion of non-detects. In this probability plot (new), the non-detects have been included and were estimated using the log-regression method. The curve on the preceding plot appears to have straightened out.

The third conclusion was that the target detection level of 10 ppq for TCDD and TCDF in effluent was reasonable. The use of 10 ppq for effluent has been somewhat controversial by industry although it was established as a goal at the beginning of the cooperative study. For combined kraft and sulfite mills, as shown in this table, the minimum is 3 ppq, the maximum is 17 ppq, the mean detection level is 7.7 and the median is 7.5 ppq. This cumulative distribution shows that about 80% of the non-detect measurements were reported at or below the target detection level of 10 ppq. In addition, after this study was completed, EPA received new data from industry which report almost all detection levels as less than 10 ppq for effluent. Reports developed by NCASI on the same data that we have from the 104-Mill Study now claim that 10 ppq is reasonable.

The next two conclusions were that the variability due to analytical error and field sampling was low as measured by lab and field duplicates. In this study, about 30% of all samples were either field or lab duplicate samples. For TCDD concentrations in effluent, there were 107 samples from 84 kraft mills of which 34 were duplicate samples from 15 mills. The number of combined lab and field dups from each of these 15 mills varied from 2 to 3 samples. (Not all mills provided duplicate samples.) There were 15 laboratory dups from 6 mills and 19 field dups from 9 mills. We were able to estimate the analytical error from the lab duplicates, and a combined estimate of field sampling and analytical variability from the field dups.

We estimated these components of variability because we planned to average the duplicates in other analyses and we wanted some indication of the effect that this averaging would have. In addition, industry has done some studies and claims that there is high analytical variability in measuring TCDD and TCDF. This claim is not supported by our analysis which uses different statistics than the industry reports. Due to NCASI's decision to restrict analyses whenever possible to one lab, there was not enough data to evaluate the variability due to inter-lab effects.

There were not enough samples that were both lab and field duplicates to evaluate the variability due to field sampling alone.

This figure shows a plot of the lab duplicate effluent TCDD measurements for kraft mills. A pair of duplicate measurements that agree perfectly would be plotted on the diagonal dashed line. To show the approximate variability, the figure also shows a 95 % confidence ellipsoid for the data. The correlation coefficient between duplicates is .98. These results were not as good for the sulfite mills. This next graph shows the lab effluent TCDD duplicates for sulfite. The correlation coefficient is .73. This next plot shows the field dups for TCDD in effluent from kraft mills. The correlation coefficient is .99. There was only one field duplicate pair from sulfite mills.

We also did an analysis of variance on the lab dups and field dups. The amount of variability due to analytical error was relatively small, 1.4%. The amount of variability due to the combination of field sampling and analytical error is also small, 0.8%.

In conclusion: 1. we could average the duplicates in other analyses; 2. there was relatively low analytical variability; 3. there was relatively low variability due to field sampling and analytical error; and so 4. we must look elsewhere for explanations of observed variability, perhaps in the processes or other factors under the control of plant management.

We were able to examine other sources of variability in the bleaching operations. In this analysis, we looked at the combined output of TCDD from effluent, sludge, and pulp. The output was adjusted for the amount of pulp production in each mill. None of the results are strong and all tend to support generally accepted working hypotheses by the industry concerning relationships among plant operations and generation of TCDD and TCDF. The data collected in this study were not intended to support an analysis of what factors increase TCDD and TCDF. However, we were able to examine three factors that were presumed to influence TCDD and TCDF levels using data collected in this study. These factors were chlorine usage, chlorine dioxide substitution for chlorine usage, and wood type used to produce the pulp.

Chlorine is important because it is used in bleaching to whiten the pulp. Different amounts of chlorine are required in bleaching to produce different products. For example, high grade writing paper requires more bleaching than diapers. Other studies have shown that TCDD and TCDF are produced mostly in the chlorination stage. The sixth conclusion of this presentation was that we found a weak positive relationship between the chlorine use and TCDD that was formed. This relationship accounts for only about 30% of the variation in the data. One problem that industry has noted is that over-chlorination even for a very short period of time leads to excess TCDD and TCDF although the overall chlorination may remain about the same as usual. This problem may be part of why the relationship isn't stronger. This plot, shows the data points overlaid by the regression line and a 90% confidence band about the estimated regression line. (explain axis) The equation is

$$\log10(\text{total TCDD}) = -0.449 + 0.010 * Cl_2 \quad R^2=32\%$$

For the seventh conclusion, we looked at the percentage of chlorine dioxide substitution for chlorine in bleaching. The chlorine dioxide substitution is used to improve effluent quality and to reduce TCDD and TCDF. Very few mills substituted for more than 30% of their chlorine usage and not all mills substituted. We found a weak relationship which accounted for at most 16% of the variation in the data. The increased use of substitution produced slight reductions in TCDD formation. The regression equation is

$$\log10(\text{total TCDD}) = 1.145 - 0.693 * \%ClO_2\text{sub} \quad R^2=16\%$$

Looking at chlorine and chlorine dioxide substitution separately is problematic. The order that these chemicals are added in the bleaching process may affect the amount of TCDD and TCDF formed. Adding the chemicals in stages instead of in one dose may reduce TCDD and TCDF. In laboratory and field studies, it has been found that there is competition between the chlorine and chlorine dioxide and this competition may increase the amount of chlorine that causes TCDD and TCDF.

We also examined the type of wood used in making the pulp. The two wood types are softwood (e.g., pine, spruce) and hardwood (e.g., oak, maple). Industry routinely applies more chlorine to pulp made from softwood to get it to the same whiteness as hardwood pulp and we did find significantly more TCDD and TCDF with the softwood.

What's next? We are continuing to collect data and study the pulp and paper industry to provide support for the development of water pollution control regulations. We are aware that the industry is dynamic and responding to the challenge of reducing and controlling TCDD and TCDF discharges. The situation represented by the data collected in 1988 is changing. Preliminary analysis of some post 1988 data indicate some changes in the amounts of TCDD and TCDF have occurred. Changes in the levels of TCDD and TCDF discharged should not, however, affect the conclusions based on the 1988 data presented here. EPA is sampling a number of mills (total of 16 to 19 mills) with 4 of these planned for long term sampling. At these sampling episodes, EPA is collecting TCDD and TCDF concentrations at more places in the process than were collected in the 104-Mill Study.

It should give us a more complete database and we may be able to evaluate more factors causing the variability in TCDD and TCDF measurements. We also mailed detailed questionnaires to these facilities. From these questionnaires, we expect additional self-monitoring data and process information. We expect to have a preliminary analysis of that data sometime before September. Eventually, we will use the data to develop effluent limits for TCDD and TCDF in the regulation.